Supporting Information for Pattern Transfer of Sub-10 nm Features via Tin-containing Block Copolymers

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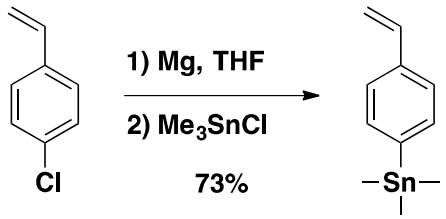
Reagents. 4-Chlorostyrene was purchased from Synquest. Magnesium, magnesium sulfate, trimethyltin chloride, trimethyl(phenyl)tin, styrene, 2-cyano-2-propyl dodecyl trithiocarbonate, 2-phenyl-2-propyl benzodithioate and 2,2'-azobis(2-methylpropionitrile) were purchased from Sigma-Aldrich. 1,2-Dibromoethane was purchased from Lancaster. 4-Methoxystyrene was purchased from Alfa Aesar. Hexane, methanol, and THF were purchased from Fisher Scientific. All chemicals above were used without further purification unless otherwise noted. 4-Chlorostyrene was purified by distillation. Monomers were passed through basic alumina columns to remove inhibitor. Tetrahydrofuran was filtered through an activated alumina column.

Instrumentation. Gel permeation Chromatography (GPC) measurements were performed on an Agilent 1100 Series Isopump and Autosampler with a Viscotek Model 302 TETRA detector. Tetrahydrofuran was used as the eluent, and the flow rate was 1 mL/min. SAXS data were conducted at Argonne National Lab on beamline 12-ID. SEM images were taken with a Zeiss Supra 40 VP. ^{1}H and ^{13}C NMR spectra were collected on a VARIAN 400 MHz instrument. Thin film IR transmission spectra were collected on a Nicolet Avatar 360 FT-IR. Molecular distributions are relative to PS standards. The dn/dc value used was 0.2027, which corresponds to the PSnS homopolymer.

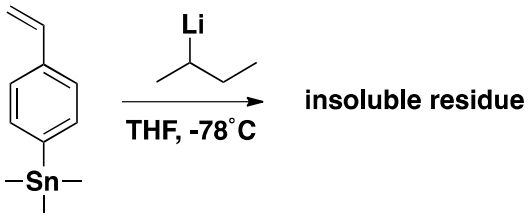


Scheme S1. Synthesis of 4-trimethylstannylstyrene (SnS).

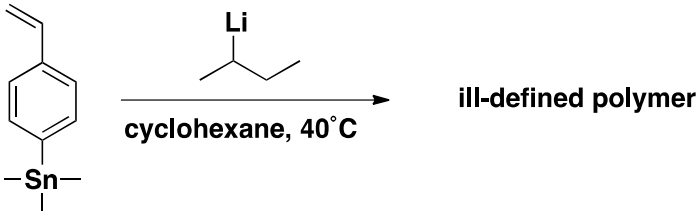
Synthesis of 4-trimethylstannylstyrene. A 1-liter 3-neck round bottom glass flask was equipped with a 250 mL addition funnel and a condenser under nitrogen. Magnesium (8.3 g, 0.341 mol), dibromoethane (0.2 mL) and anhydrous tetrahydrofuran (50 mL) were added to the flask. The solution was stirred at 60 °C for 1.5 hours. A solution of 4-chlorostyrene (31.5 g, 0.227 mol) in tetrahydrofuran (150 mL) solution was added via addition funnel slowly for 1 hr. under a constant flow of nitrogen gas. The solution was stirred at 60 °C for additional 1.5 hr. The solution was cooled gradually at 0 °C. Trimethylstannyl chloride (43.0 g, 0.216 mol) in tetrahydrofuran (30 mL) solution was added to the solution slowly for 0.5 hr. The solution was warmed to room temperature and stirred for an additional 1.5 hr. The solution was cooled back to 0˚C and water (100 mL) was added slowly to the solution. The solution was warmed to room temperature and hexane (200 mL) was added. The solution was stirred for 15 min and filtered. The organic layer was separated and washed two times with water (30mL), and then dried over magnesium sulfate, and concentrated via rotary evaporation. The crude product was purified by distillation at 1 Torr and 105 °C to give 44.4 g of 4-trimethylstannylstyrene as a colorless liquid. GC spectra showed 99.5% purity. The yield of the reaction was 73 %. ^{1}H NMR ($CDCl_3$): δ = 7.39 (m, 1H), 6.70 (dd, J = 20 Hz, J = 12 Hz, 1H), 5.77 (d, J = 20 Hz, 1H), 5.24 (d, J = 12 Hz, 1H), 0.28 (t, J = 24 Hz, 9H). ^{13}C NMR ($CDCl_3$): δ = 142.09, 137.47, 136.94, 136.00, 125.75, 113.79, -9.57. HRMS (CI) m/z for $[M]^+$ calcd for $C_{11}H_{16}Sn$ 268.0274; found for 268.0283(^{120}Sn), also found for 264.0256 (^{116}Sn) and 266.0273(^{118}Sn).

Anionic polymerization attempts:

The anionic procedures used herein have been reported elsewhere[1].



Scheme S2. Anionic polymerization attempt in tetrahydrofuran.



Scheme S3. Anionic polymerization attempt in cyclohexane.

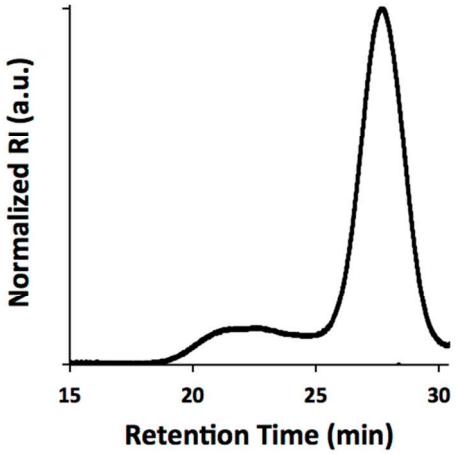
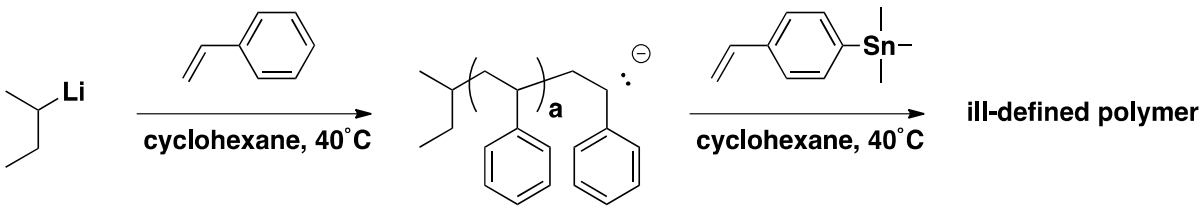


Figure S1. SEC trace of the polymer resulting from Scheme S3. The distribution of molecular weights was bimodal. The major peak had an M_n = 4.6 kDa and $Đ$ = 1.30 whereas the minor peak had M_n = 59.6 kDa and Đ = 1.78. This is indicative of an uncontrolled polymerization.



Scheme S4. Attempt to polymerize poly(styrene-*block*-4-trimethylstannylstyrene) via anionic polymerization.

Living polystyrene was synthesized according to scheme S4. The polystyrene aliquot was well-defined (M_n = 22.9 kDa, Đ = 1.05). Addition of the SnS to the living anion resulted in an ill-defined polymer. The SEC chromatographs of the aliquot and BCP are shown in Figure S2.

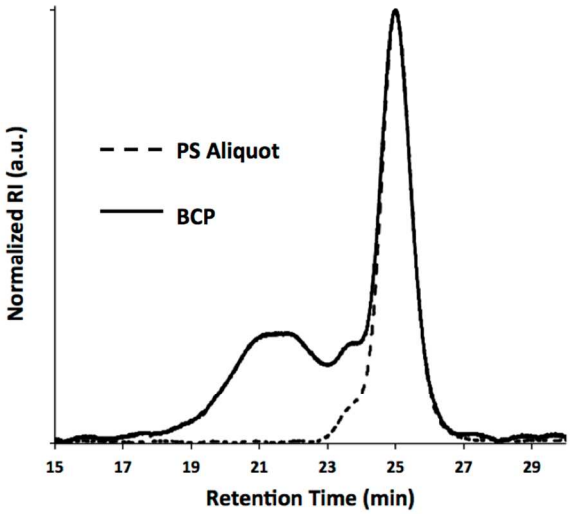
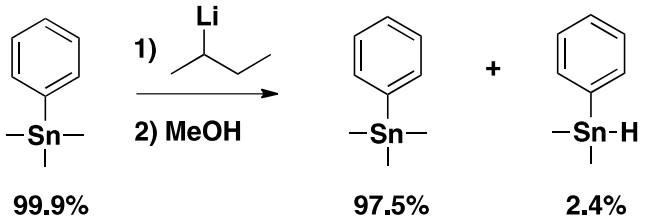


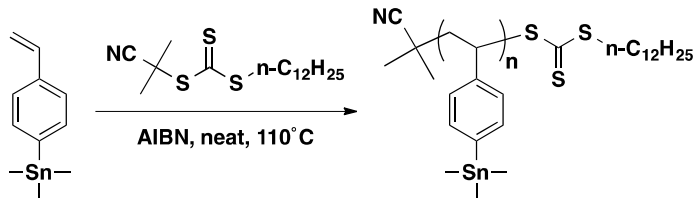
Figure S2. SEC traces of the polystyrene aliquot (dashed line) and resulting BCP formed after the addition of SnS (solid line).



Scheme S5. Reaction of trimethyl(phenyl)tin with *sec*-butyllithium followed by quenching with methanol.

A reaction vessel of trimethyl(phenyl)tin (0.2 g, 1 eq) was degassed with two freeze-pump-thaw cycles and backfilled with nitrogen. The reaction vessel was placed in an oil bath set at 40˚C. Then, *sec*-butyllithium (60 µL of 1.4 M in hexanes) was added and stirred for two hours. The reaction was quenched with methanol and analyzed by GC.

Poly(4-trimethylstannylstyrene) homopolymer synthesis:



Scheme S6. Synthesis of poly(4-trimethylstannylstyrene) (PSnS) by RAFT polymerization.

Synthesis of poly(4-trimethylstannyl styrene) (PSnS). Method A: A mixture of 4-trimethylstannylstyrene (3.30 g, 12.4 mmol), 2-cyano-2-propyldodecyltrithiocarbonate (19.0 mg, 0.055 mmol), and 2,2'-azobis(2-methylpropionitrile) (1.1 mg, 0.006 mmol) was added to a 25 mL round bottom flask with a condenser and degassed by two freeze-pump-thaw cycles. The solution was stirred at 110 °C under nitrogen for 24 hours. The reaction mixture was dissolved in tetrahydrofuran (3 mL), precipitated into methanol (250 mL) twice, and dried to give PSnS as a white powder (2.15 g, 65% yield). The dn/dc value was determined to be 0.2027 by GPC.

Synthesis of poly(4-trimethylstannyl styrene) (PSnS). Method B: A mixture of 4-trimethylstannyl styrene (3.02 g, 11.3 mmol), and 2-cyano-2-propyldodecyltrithiocarbonate (12.5 mg, 0.036 mmol) was added to a 250 mL round bottom flask and degassed by two freeze-pump-thaw cycles. The solution was stirred at 110 °C under nitrogen, and *tert*-butyl peroxybenzoate (0.3 mg, 0.002 mmol) dissolved in 0.5 g *p*-xylenes was slowly added to the solution with syringe pump for 3 hours and then stirred for 21 hours. The reaction mixture was dissolved in tetrahydrofuran (20 mL), precipitated into methanol (500 mL) twice, and dried to give PSnS a white powder (1.00 g, 33% yield).

Table S1. Homopolymer synthesis details.

Entry	Method	SnS/Initiator*	Time (hr)	M_n (kDa)**	$Đ$	Yield
1	B	315	24	36.3	1.12	33%
2	A	225	19	30.9	1.12	65%
3	A	110	22	15.4	1.20	50%
4	A	97	23	13.9	1.13	74%
5	A	93	20	12.9	1.04	79%
6	A	76	23	11.8	1.01	75%
7	A	75	18	10.8	1.04	67%
8	A	56	17	7.6	1.04	72%
9	A	37	22	5.1	1.07	77%

*Mol ratio

**Determined by SEC using a dn/dc value of 0.2027

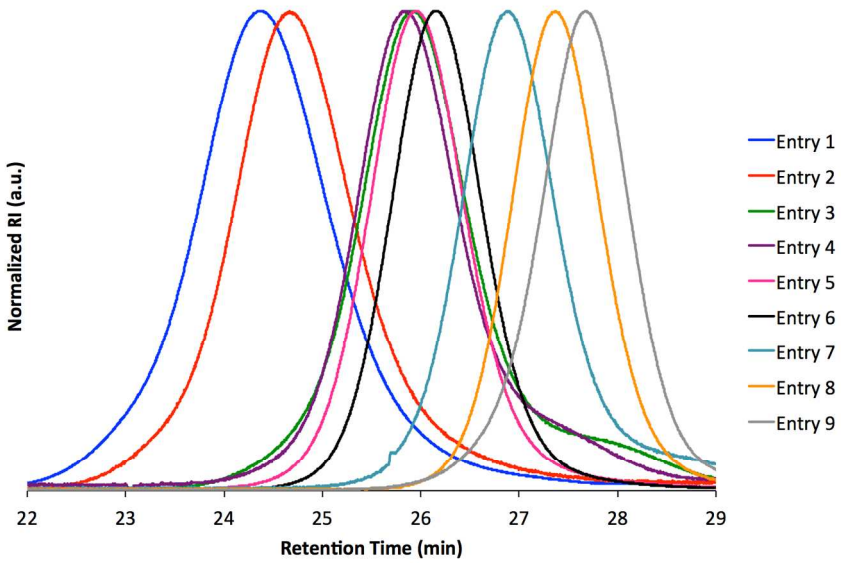


Figure S3. SEC traces of the poly(4-trimethylstannylstyrene) homopolymers synthesized via RAFT. The entries correspond to Table S1.

Synthesis of poly(4-trimethylstannyl styrene)-*b*-polystyrene (PSnS-PS). A mixture of PSnS (0.760 g), styrene (1.527 g, 14.7 mmol), and 2,2'-azobis(2-methylpropionitrile) (0.2 mg, 0.001 mmol) was added to 25 mL round bottom flask with a condenser, and then were degassed by two freeze-pump-thaw cycles, was stirred at 110 °C under nitrogen for 7 hours. The solidified reaction mixture was dissolved in tetrahydrofuran (5 mL) and precipitated into methanol (100 mL) two times, and then dried to give PSnS-PS (1.21 g) as white powder. The M_w and Đ were 85.4 kDa and 1.31, respectively.

Synthesis of Poly(4-trimethylstannylstyrene)-*b*-polymethoxystyrene (PSnS-*b*-PMOST). A mixture of PSnS (0.392 g), 4-methoxystyrene (0.745 g, 5.55 mmol), and 2,2'-azobis(2-methylpropionitrile) (0.7 mg, 0.004 mmol) was added to 25 mL round bottom flask with a condenser and was degassed by two freeze-pump-thaw cycles. Then, the solution was stirred at 110 °C under nitrogen for 2 hours. The solidified reaction mixture was dissolved in tetrahydrofuran (2 mL) and precipitated into methanol (100 mL) two times, and dried to give PSnS-PMOST (0.53 g) as white powder. The M_w was calculated to be 21.4 kDa, and the Đ of 1.18.

Removal of RAFT end groups. The RAFT end groups were removed for thin film studies using a previously reported method[2]. Approximately 1 g of BCP was dissolved in toluene with 20 eq. of AIBN. The solution was heated to 80˚C for 8 hrs. The solution was cooled to room temperature, precipitated in methanol, filtered and dried *in vacuo*.

Table S2. Additional block copolymer synthetic details and characterization data

				BCP				
Sample	PSnS M_n (kDa)*	(Mon2/ PSnS)**	Time (hr)	Yield	PS or PMOST M_n (kDa)***	Đ	T_g (˚C)	T_d (˚C)
PSnS-PS_{34}	36.3	2.0	7	53%	24.5	1.31	107, 115	297
PSnS-PS_{dis}	10.8	1.5	2.5	51%	7.1	1.24	105, 115	260
PSnS-$PMOST_{20}$	11.8	2.0	2	60%	9.1	1.07	100, 115	261
PSnS-$PMOST_{18}$	10.8	2.0	2	46%	8.5	1.18	106, 114	257

*Determined by SEC

** Mon2 is either styrene or 4-methoxystyrene. Mass ratio of Mon2 to PSnS macroinitiator.

***Determined by NMR

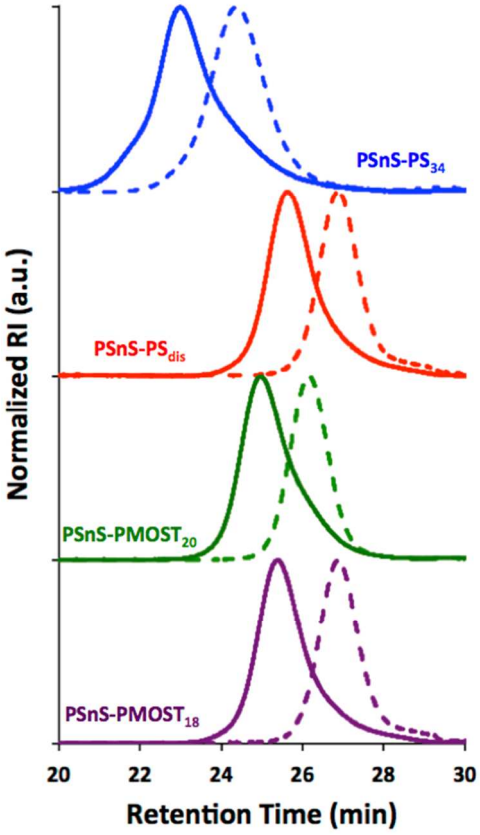


Figure S4. SEC traces of the PSnS-PS or PSnS-PMOST (solid lines) and their corresponding homopolymers (dashed lines).

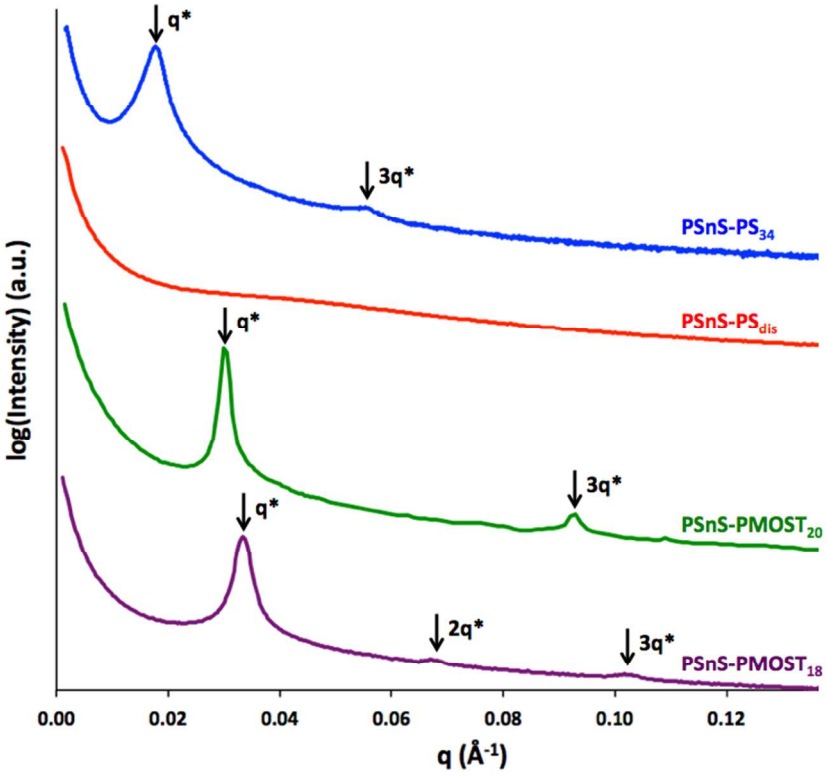


Figure S5. Synchrotron small angle x-ray scattering profiles of the block copolymers listed in Table 2.

Thin Film Preparation:

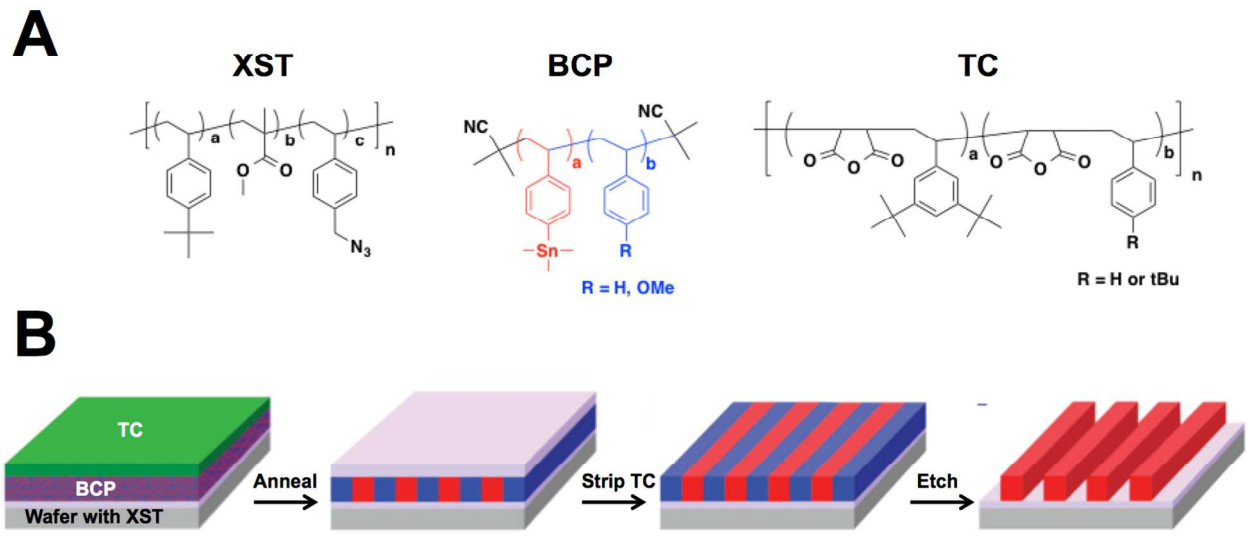


Figure S6. **(A)** Materials used in the present study. **(B)** Schematic of the process flow to develop BCP features for topdown imaging.

Neutral surface screening. Neutral top and bottom interfaces were found using previously reported materials and methodology[1,3].

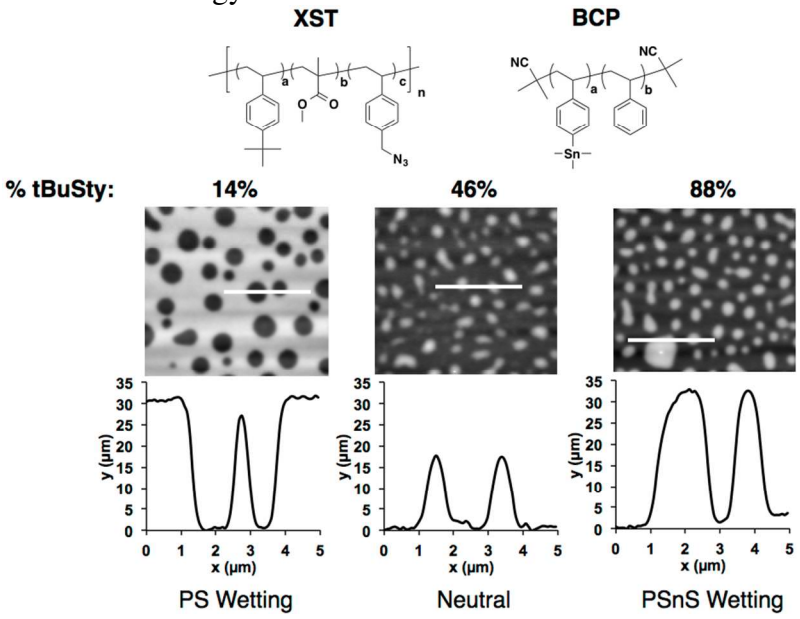


Figure S7. Atomic force micrographs of the surface topography formed after annealing PSnS-PS_{34} on different XST surface treatments. The height profiles collected using tapping mode are shown. The BCP film thicknesses are between 1-1.5 L_0 and were baked at 180˚C for 10 minutes. The "half" islands formed on the 46% tBuSty XST are indicative of a neutral surface.

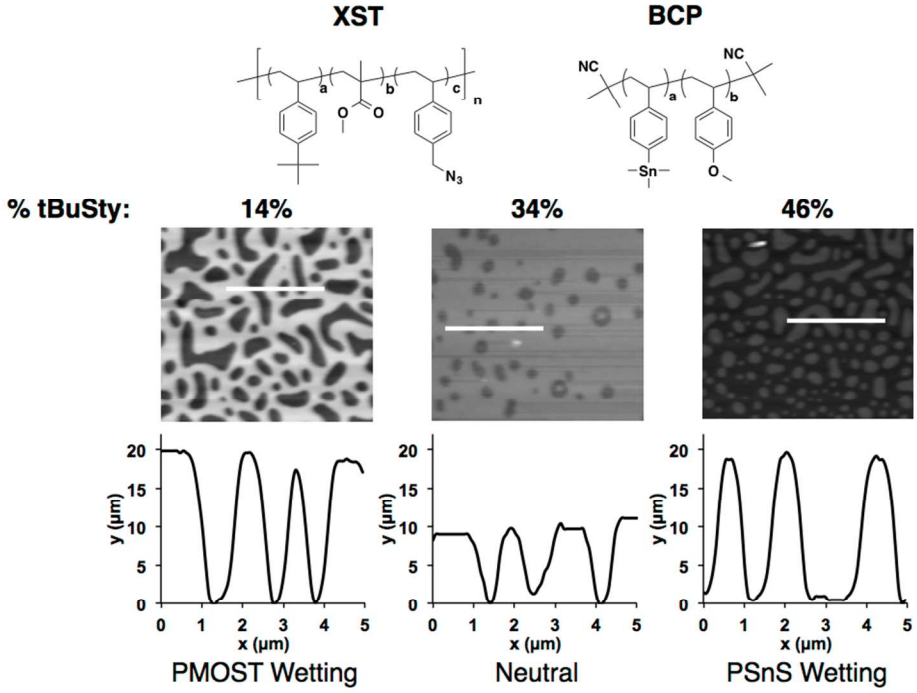


Figure S8. Atomic force micrographs of the surface topography formed after annealing PSnS-$PMOST_{20}$ on different XST surface treatments. The height profiles collected using tapping mode are shown. The BCP film thicknesses are between 1-1.5 L_0 and were baked at 180˚C for 10 minutes. The "half" holes formed on the 34% tBuSty XST are indicative of a neutral surface.

Table S3. Composition of the neutral interfaces

	XST Composition (%)*			TC Composition (%)*			
BCP	tBuSty	Sty	VBzAz	MA	tBuSty	ditBuSty	Sty
PSnS-PS	46	46	8	52	0	12	36
PSnS-PMOST	34	60	6	50	50	0	0

*determined by combustion

tBuSty = 4-*tert*-butylstyrene
Sty = styrene
VBzAz = 4-vinylbenzylazide
MA = maleic anhydride
ditBuSty = 3,5-di-*tert*-butylstyrene

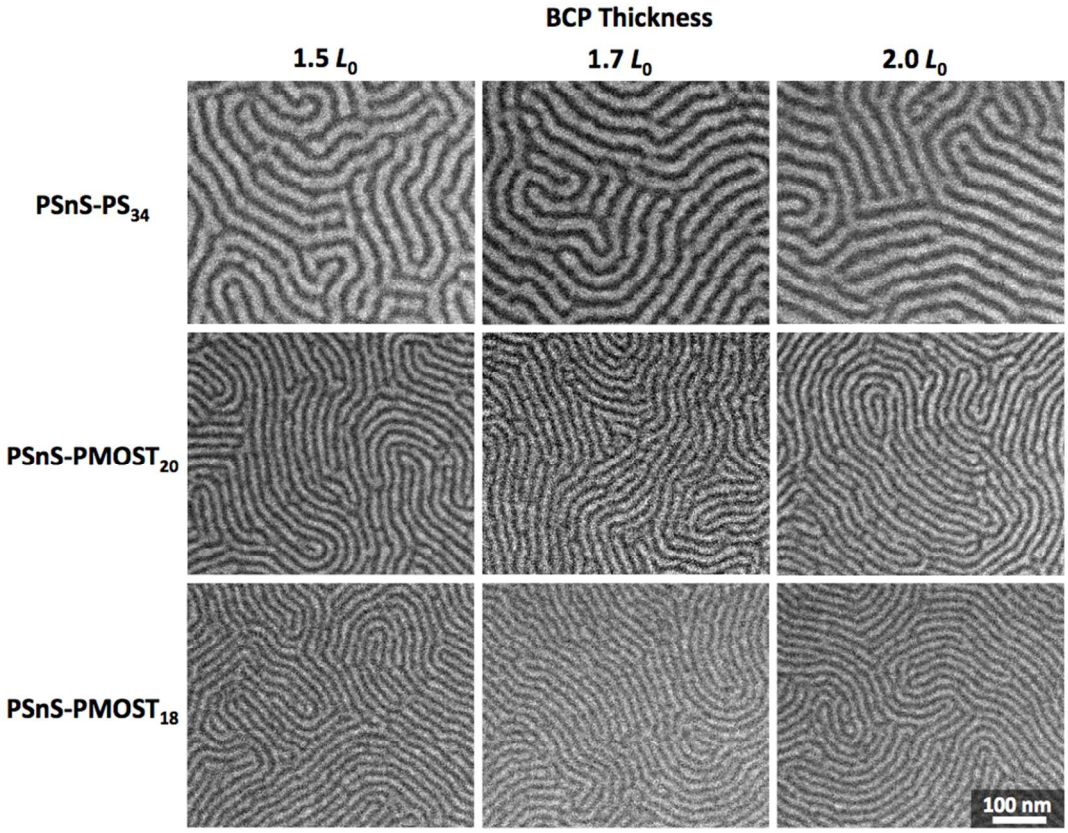


Figure S9. Top down SEM micrographs of BCP self-assembly. Samples were annealed at 180˚C for 10 min. The scale bar is valid for all micrographs.

Plasma Etching

Etch Chamber. Plasma etching was performed on a commercial 300mm capacitively coupled plasma reactor, Lam Research Exelan® Flex45™, which contains confined plasma technology and multisource RF frequencies applied to the bottom electrode.

Etch Rate and Pattern Transfer Tests. For etch rate and BCP pattern transfer tests, coupons (2000 mm^2) coated with either homopolymer or assembled BCP patterns were thermally pasted (Type 120 Silicone, Wakefield Solutions) onto the center of 300mm 248nm DUV resist carrier wafers. SiO_2 coupons were prepared in a similar fashion. For pattern transfer tests using BCP masks, CF_4-rich plasma chemistry was used for all of the samples. For the largest pitch BCP sample, CHF_3 was added to the CF_4. For the smallest pitch samples, Ar and O2 were added and the gas ratios were adjusted in order to obtain an acceptable profile.

Surface Analysis

Instrumentation. Angle resolved x-ray photoelectron spectroscopy (ARXPS) was used to explore post etch surface chemistry modifications of BCPs. XPS spectra were collected using a Thermo Fisher Scientific Theta 300 ARXPS instrument utilizing a monochromatic Al kα x-ray source (hν=1486.6eV) and an electron energy analyzer operating in a high energy resolution mode with a constant pass energy of 50eV.

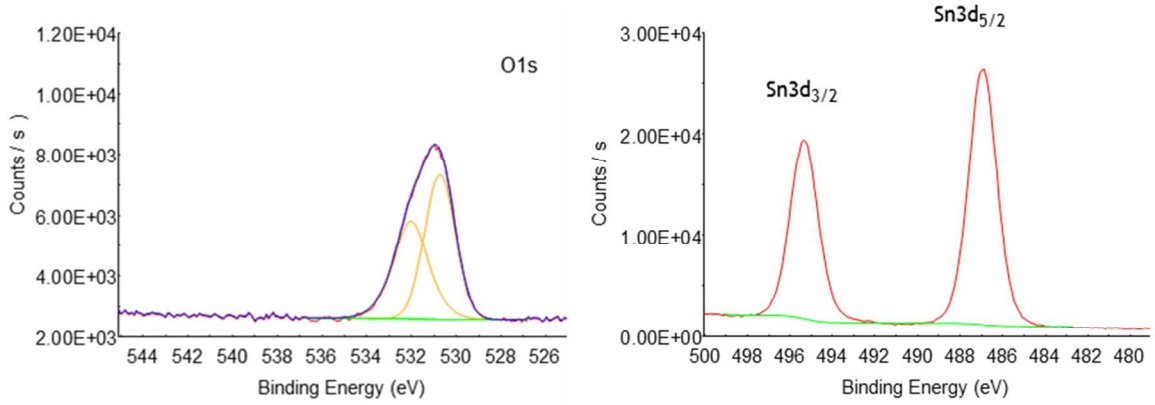


Figure S10. High energy resolution O1s and Sn3d XPS spectra provide additional insight about surface chemistry after CO_2 etch process. Binding energies and peak shapes are consistent with the formation of SnO_x species at the surface.

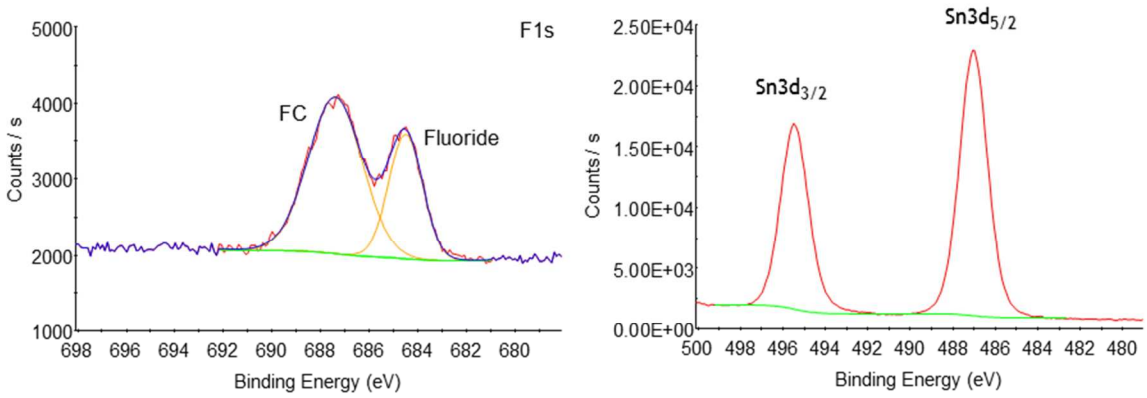


Figure S11. High energy resolution F1s and Sn3d XPS spectra are shown after the 2nd CF_4/CHF_3 etch step. Evidence of fluorocarbon and metal fluroides are observed. Binding energies and peak shapes are consistent with SnF_x, SnO_xF_y, and SnO_x formation.

References

(1) Maher, M. J.; Bates, C. M.; Blachut, G.; Sirard, S.; Self, J. L.; Carlson, M. C.; Dean, L. M.; Cushen, J. D.; Durand, W. J.; Hayes, C. O.; Ellison, C.J.; Willson, C.G. *Chem. Mater.* **2014**, *26*, 1471–1479.

(2) Bang, J.; Bae, J.; Löwenhielm, P.; Spiessberger, C.; Given-Beck, S. A.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2007**, *19*, 4552–4557.

(3) Kim, S.; Bates, C. M.; Thio, A.; Cushen, J. D.; Ellison, C. J.; Willson, C. G.; Bates, F. S. *ACS Nano* **2013**, *7*, 9905–9919.